

10/524366

Silicas

The invention relates to silanised, structurally modified, pyrogenically produced silicas, a process for the production thereof and their use.

- 5 Silanised silicas are used as thickeners, such as e.g. for water-thinnable lacquers and resins, such as e.g. epoxy resins.

From EP 0 672 731 B1, silanised, pyrogenically produced silicas are known, which are characterised in that the
10 pyrogenically produced silicas are treated with a compound from the group $(RO)_3SiC_nH_{2n+1}$, wherein $n=10$ to 18 and $R=$ short-chained alkyl radicals. For example, the pyrogenically produced silicas have been treated with the compound $(CH_3O)_3SiC_{16}H_{33}$ (hexadecyltrimethoxysilane) or with
15 the compound $(CH_3O)_3SiC_{18}H_{37}$ (octadecyltrimethoxysilane).

The production of the silanised, pyrogenically produced silicas takes place in that the pyrogenically produced silicas are placed in a mixer, the silicas are sprayed, optionally first with water and then with the compound from
20 the group $(RO)_3SiC_nH_{2n+1}$ while mixing intensively, mixed for a further 15 to 30 minutes and then tempered at a temperature of 100 to 160°C for a period of 1 to 3 hours.

The invention provides silanised, structurally modified, pyrogenically produced silicas characterised by groups
25 fixed on the surface, the groups being alkylsilyl (SiC_nH_{2n+1}) , with $n=2 - 18$, preferably octylsilyl and/or hexadecylsilyl.

The silica according to the invention can have the following physico-chemical characteristics:

- BET-surface area m²/g: 25 - 400
- Average size of the
primary particles nm: 5 - 50
- pH value: 3 - 10
- 5 Carbon content %: 0.1 - 25
- DBP value %: The DBP value is at least 10%
lower than the DBP value of the
corresponding silanised, non-
structurally modified silica. With
10 very marked structural
modification, the structure can be
broken down in such a way that the
DBP value can no longer be
determined.
- 15 A silica produced by a high-temperature hydrolysis route
from SiCl₄ + H₂ and O₂ can be used as the pyrogenically
produced silica.
- In particular, a silica produced by high temperature
hydrolysis having the following physico-chemical
20 characteristics can be used:

- 1) based on DIN 66131
- 2) based on DIN ISO 787/XI, JIS K 5101/18 (not sieved)
- 3) based on DIN ISO 787/II, ASTM D 280, JIS K 5101/21
- 5 4) based on DIN 55 921, ASTM D 1208, JIS K 5101/23
- 5) based on DIN ISO 787/IX, ASTM D 1208, JIS K 5101/24
- 6) based on DIN ISO 787/XVIII, JIS K 5101/20
- 7) based on the substance dried for 2 hours at 105°C
- 8) based on the substance ignited for 2 hours at 1000°C
- 9) HCl content is a component of the loss on ignition

Pyrogenic silicas of this type are known. They are described, *inter alia*, in:

Winnacker-Küchler, Chemische Technologie, volume 3 (1983), 4th edition, page 77 and

- 5 Ullmanns Encyklopädie der technischen Chemie, 4th edition (1982), volume 21, page 462.

The pyrogenically produced silicas are treated with a compound from the group $(RO)_3SiC_nH_{2n+1}$, wherein $n = 2$ to 18 and R = alkyl, such as e.g. methyl, ethyl or similar.

- 10 In particular, the following compounds can be used:

Silane I $(CH_3O)_3SiC_{16}H_{33}$ (hexadecyltrimethoxysilane)

Silane II $(CH_3O)_3SiC_8H_{17}$ (octyltrimethoxysilane)

- The silicas according to the invention can be produced in that the pyrogenically produced silicas are placed in a mixer, the silicas are sprayed, optionally first with water and then with the compound (organosilane) from the group $(RO)_3SiC_nH_{2n+1}$ while mixing intensively, mixed for a further 15 to 30 minutes and then tempered at a temperature of 100 to 160°C for a period of 1 to 3 hours, structurally modified and/or optionally post-ground. A further tempering can optionally take place after the structural modification and/or post-grinding.

- The structural modification can take place e.g. with a ball mill or a continuously operating ball mill. The post-grinding can take place e.g. using an air-jet mill or pin mill. The tempering can take place batchwise, e.g. in a drying cupboard, or continuously, e.g. in a fluidised bed. The tempering can take place under protective gas, e.g. nitrogen.

- 30 The water used can be acidified with an acid, e.g. hydrochloric acid, down to a pH value of 7 to 1.

The organosilane used can be dissolved in a solvent, such as e.g. ethanol.

The tempering can be performed in a protective gas atmosphere, such as e.g. under nitrogen.

- 5 The pyrogenically produced silicas according to the invention silanised with silane I have the physico-chemical characteristics listed in Table 2 before structural modification:

Table 2[illegible]

The silanised, structurally modified, pyrogenically produced silicas according to the invention can be used to improve scratch resistance in lacquers.

5 Examples

The pyrogenically produced silicas used have the physico-chemical characteristics listed in Table 1.

As organosilanes, the following compound with the general formula $(RO)_3SiC_nH_{2n+1}$ is used:

10 (Silane I) $(CH_3O)_3SiC_{16}H_{33}$

The silica is placed in a mixer and sprayed first with water and then with organosilane, mixing intensively.

15 When the spraying is complete, stirring is continued for a further 15 to 30 minutes and then the mixture is tempered for 1 to 3 hours at 100 to 160°C. The tempering can also take place under protective gas, e.g. nitrogen.

The individual reaction conditions can be taken from Table 3.

20 The physico-chemical characteristics of the silanised silicas obtained are listed in Table 4.

Table 3

Example	Aerosil	Silane	Silane quantity (g/100 g Aerosil)	Water quantity (g/100 g Aerosil)	Ethanol quantity (g/100 g Aerosil)	Tempering period (h)	Tempering temperature (°C)
1	A 300	Silane I	1	0	9	2	120
2	A 200	Silane I	2.5	0	0	2	140
3	A 200	Silane I	20	5	0	2	140
4	A 200	Silane I	10	2.5	0	2	140
5	A 200	Silane I	5	1.25	0	2	140
6	A 200	Silane I	2.5	1.25	0	2	140

Table 4

Example	pH value	Tamped density (g/l)	C content (%)	Surface area (m ² /g)	Loss on drying (%)	Loss on ignition (%)
1	4.3	50	1.3	253	0.4	1.8
2	4.4	49	1.7	176	0.3	2.5
3	4.6	68	10.1	116	0.6	12.7
4	4.5	72	5.7	144	0.6	7.1
5	4.7	52	2.6	167	0.6	3.4
6	4.5	51	1.9	171	0.7	2.5

Production and physico-chemical properties of the silicas according to the invention

Production of the silicas according to the invention:

5 The silicas, which can be produced as described in EP 0 672 731, are then structurally modified by mechanical action and possibly post-ground in a mill. A tempering can possibly take place after the structural modification and/or post-grinding.

10 The structural modification can take place e.g. with a ball mill or a continuously operating ball mill. The post-grinding can take place e.g. using an air-jet mill or pin mill. The tempering can take place batchwise, e.g. in a drying cupboard, or continuously, e.g. in a fluidised bed. The tempering can take place under protective gas, e.g.
15 nitrogen.

Table 5 Overview of the production of the comparative silicas and the silicas according to the invention (Examples)

Designation	Surface-fixed group	Structural modification	Post-grinding after structural modification	Tempering after post-grinding
Comparative silica 1	Hexadecylsilyl	No	-	-
Comparative silica 2	Octylsilyl	No	-	-
Silicas 1	Hexadecylsilyl	Yes	No	No
Silicas 2	Octylsilyl	Yes	Yes	No
Silicas 3	Hexadecylsilyl	Yes	Yes	Yes
Silicas 4	Octylsilyl	Yes	No	Yes
Silicas 5	Octylsilyl	Yes	Yes	No
Silicas 6	Hexadecylsilyl	Yes	Yes	No
Silicas 7	Hexadecylsilyl	Yes	Yes	No
Silicas 8	Hexadecylsilyl	Yes	No	No
Silicas 9	Octylsilyl	Yes	Yes	No
Silicas 10	Octylsilyl	Yes	No	No
Silicas 11	Octylsilyl	Yes	Yes	No
Silicas 12	Octylsilyl	Yes	No	No

Table 6: Physico-chemical data of the silicas according to the invention (Examples) and the comparative silicas

Designation	Tamped density [g/l]	Loss on drying [%]	Loss on ignition [%]	pH value	C content [%]	DBP adsorption [%]	BET specific surface area [m ² /g]
Comparative silica 1	57	0.5	1.8	4.6	1.2	302	195
Comparative silica 2	51	0.6	6.8	5.3	5.4	263	175
Silicas 1	137	0.7	1.9	4.9	1.3	217	193
Silicas 2	112	0.7	7.0	5.8	5.5	145	175
Silicas 3	118	0.7	2.3	5.1	1.3	228	176
Silicas 4	163	0.9	6.7	5.3	5.4	134	176
Silicas 5	114	0.5	7.1	6.0	5.4	142	175
Silicas 6	113	1.3	2.2	5.1	1.4	221	193
Silicas 7	123	0.7	2.6	6.0	1.4	208	197
Silicas 9	146	1.1	2.3	5.8	1.4	182	195
Silicas 9	240	0.8	6.7	4.8	5.3	87	169
Silicas 10	322	0.3	6.9	6.0	5.3	Could not be determined	172
Silicas 11	204	0.7	6.4	5.7	5.4	101	173
Silicas 12	276	0.3	6.6	6.6	5.3	Could not be determined	168

Application examplesExample 1:

For the investigation of the improvement in scratch resistance, a conventional 2-component polyurethane lacquer was used. The formulation of the lacquer and its production, including application, are summarised below:

Formulation:

Millbase	Parts by wt.
Acrylic resin, 50% in xylene/ethylbenzene 3:1	53.3
Butyl acetate 98%	6.7
Xylene	6.7
Silica	5.0
Σ	71.7
Lacquer make-up	
Acrylic resin, 50% in xylene/ethylbenzene 3:1	1.1
Xylene	12.2
Ethoxypropyl acetate	1.5
Butyl glycol acetate	1.5
Butyl acetate 98%	-
Aliphatic polyisocyanate, approx. 75% in 1-methoxypropyl-2-acetate/xylene 1:1	17.0
Σ	105.0

Binder concentration:	40%
Silica calculated on the basis of millbase (solids):	18.8%
Silica calculated on the basis of lacquer (total):	5.0%
Silica calculated on the basis of lacquer (solids):	12.5%

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Production and application of lacquers

The binder is mixed with the solvents. Then, for the purpose of predispersion, the silica is incorporated into this mixture with the high-speed mixer (disk Ø 45 mm) and
10 predispersed for 5 min at 2000 rpm. The mixture is dispersed in a laboratory pearl mill for 30 min at 2500 rpm and 60% pump capacity using glass beads (Ø approx. 1 mm). The millbase is tested with a grindometer, 25 µm, according to DIN ISO 1524. It must be smaller than 10 µm.

15 The conversion of the millbase to lacquer takes place in accordance with the formulation, the components being mixed at 2000 rpm with a vane agitator. The hardener is incorporated in the same way.

20 After adjusting the lacquers to spray viscosity in accordance with DIN 53411, the lacquers are applied to black lacquered metal sheets, e.g. DT 36 (from Q-Panel), by spray application (coat thickness about 40-50 µm). After spraying, the metal sheets are dried for 24 h at room temperature and then for 2 h in a drying oven at 70°C.

Scratch tests:

The metal sheets are abraded with a quartz/water slurry (100 g water + 1 g Marlon A 350, 0.25% + 5 g Sikron F500) and with a CaCO₃/water mixture (100 g water + 1 g Marlon A 350, 0.25% + 5 g Millicarb BG) using an abrasion and washing resistance tester (Erichsen, brush with hog's bristles). The gloss before and 10 min after the abrading is determined with a reflectometer (20° irradiation angle).

Table 7: Summary of the properties of the liquid lacquers relevant in terms of lacquer technology, and of the applied and dried films.

	Comparative silica 1	Silica 7	Silica 8	Reference without silica	Comparative silica 2	Silica 9	Silica 11	Reference without silica
Grindometer value [μm]	< 10	< 10	< 10	< 10	< 10	< 10	< 10	/
Viscosity (millibase) [mPas] 6 Rpm 60 Rpm	409 407	210 210	220 212	/ /	5670 1260	935 409	832 407	/ /
Viscosity (lacquer + hardener) [mPas] 6 rpm 60 rpm	120 113	80 82	80 82	60 61	446 194	195 146	175 144	55 64
Flow	poor fine cracks	OK	OK	OK	Orange peel effect	OK	OK	OK
Scratch resistance								
20° reflectometer value before scratching	81	89.5	89.1	91.3	38	85.5	85.3	91.7
Haze before scratching	101	9	12	2	423	18	19	2
Black value My	272	286	286	291	260	283	282	294
40 strokes with Sikron F 500 residual gloss [%]	83.4	88.5	90.7	51.8	/	80.4	84.3	56.1

The silicas 7 + 8 and 9 + 11 according to the invention can be used in high concentrations without impairing the appearance of the lacquer surface owing to their substantially lower rheological efficiency compared with comparative silica 1 + 2. In addition, the silicas according to the invention display a substantial improvement in scratch resistance of the lacquer surface.

Example 2

In this example the influence of the structural modification was investigated on the basis of a high solids 2-component PU clear lacquer. The formulation of the lacquer and its production, including application and testing, are summarised below:

Formulation:

Millbase	Parts by wt.
Acrylic copolymer, mod. with synthetic fatty acids, 70% in n-butyl acetate	61.0
Butyl acetate 98%	7.3
Methoxypropyl acetate	1.7
Solvesso 100	2.0
Xylene	2.0
Baysilon OL 17, 10% in xylene (silicone oil)	0.7
Silica	5.0
Σ	79.7
Lacquer make-up (hardener)	
Aliphatic polyisocyanate, 90% in n-butyl acetate	22.3
Butyl acetate 98%	2.0
Solvesso 100	1.0
Σ	105.0

Binder concentration: 62.8%
Silica calculated on the basis of millbase (solids): 11.7%
Silica calculated on the basis of lacquer (total): 5.0%
Silica calculated on the basis of lacquer (solids): 8.0%

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Production and application of the lacquers

The binder is mixed with the solvents. Then, for the purpose of predispersion, the silica is incorporated into this mixture with the high-speed mixer (disk Ø 45 mm) and
10 predispersed for 5 min at 2000 rpm. The mixture is dispersed in a laboratory pearl mill for 30 min at 2500 rpm and 60% pump capacity using glass beads (Ø approx. 1 mm). The millbase is tested with a grindometer, 25 µm, in accordance with DIN ISO 1524. It must be smaller than
15 10 µm.

The conversion of the millbase to lacquer takes place in accordance with the formulation, the components being mixed with a vane agitator at 2000 rpm. The hardener is incorporated in the same way.

20 After adjusting the lacquers to spray viscosity in accordance with DIN 53411, the lacquers are applied to black lacquered metal sheets, e.g. DT 36 (from Q-Panel), by spray application (coat thickness about 40-50 µm). After spraying, the metal sheets are dried for 24 h at room
25 temperature and then for 2 h in a drying oven at 70°C.

Scratch tests:

The metal sheets are abraded with a quartz/water slurry (100 g water + 1 g Marlon A 350, 0.25% + 5 g Sikron F500) using an abrasion and washing resistance tester (Erichsen,
30 brush with hog's bristles). The gloss before and 10 min after the abrading is determined with a reflectometer (20° irradiation angle).

Table 8: Summary of the properties of the liquid lacquers relevant in terms of lacquer technology, and of the applied and dried films.

	Comparative silica 1	Silica 7	Silica 8	Reference without silica
Bulk density [g/l]	50	146	123	/
Grindometer value [μm]	< 10	< 10	< 10	/
Viscosity (millbase) [mPas]				
6 rpm	767	376	376	205
60 rpm	717	359	361	205
Viscosity (lacquer + hardener) [mPas]				
6 rpm	459	279	281	120
60 rpm	399	272	274	120
Flow	poor (fine "cracks")	OK	OK	OK
Scratch resistance				
20° reflectometer value before scratching	82.3	86.5	86.3	88.2
Haze before scratching	3	4	4	2
Black value My	275	283	282	292
40 strokes with Sikron F 500 residual gloss [%]	63.2	78.2	75.4	30.2

- 5 The silicas 7 + 8 according to the invention can be used in high concentrations without impairing the appearance of the lacquer surface owing to their substantially lower rheological efficiency compared with comparative silica 1. In addition, the silicas according to the invention display
- 10 a substantial improvement in the scratch resistance of the lacquer surface.

Example 3:

For the investigation of the improvement of the scratch resistance, a conventional 2-component polyurethane lacquer was used. The formulation of the lacquer and its
 5 production, including its application, are summarised below:

Formulation

Millbase	Parts by wt.
Acrylic copolymer, mod: with synthetic fatty acids, 60% solution	43.4
Butyl acetate 98%	17.8
Xylene	3.9
Silica	5.0
Σ	70.7
Lacquer make-up	
Xylene	11.3
Ethoxypropyl acetate	3.4
Butyl glycol acetate	1.6
Aliphatic polyisocyanate, approx. 75% in 1-methoxypropyl-2-acetate/xylene 1:1	18.6
Σ	105.0

Binder concentration: 40%

10 Silica calculated on the basis of millbase (solids): 19.2%

Silica calculated on the basis of lacquer (total): 5.0%

Silica calculated on the basis of lacquer (solids): 12.5%

Production and application of the lacquers

15 The binder is mixed with the solvents. Then, for the purpose of predispersion, the silica is incorporated into this mixture with the high-speed mixer (disk Ø 45 mm) and predispersed for 5 min at 2000 rpm. The mixture is

dispersed in a laboratory pearl mill for 30 min at 2500 rpm and 60% pump capacity using glass beads (\varnothing approx. 1 mm). The millbase is tested with a grindometer, 25 μm , in accordance with DIN ISO 1524. It must be smaller than

5 10 μm .

The conversion of the millbase to lacquer takes place in accordance with the formulation, the components being mixed with a vane agitator at 2000 rpm. The hardener is incorporated in the same way.

10 After adjusting the lacquers to spray viscosity in accordance with DIN 53411, the lacquers are applied to black lacquered metal sheets, e.g. DT 36 (from Q-Panel), by spray application (coat thickness about 40-50 μm). After spraying, the metal sheets are dried for 24 h at room

15 temperature and then for 2 h in a drying oven at 70°C.

Scratch tests:

The metal sheets are abraded with a quartz/water slurry (100 g water + 1 g Marlon A 350, 0.25% + 5 g Sikron F500) using an abrasion and washing resistance tester (Erichsen,

20 brush with hog's bristles). The gloss before and 10 min after the abrading is determined with a reflectometer (20° irradiation angle).

Table 9: Summary of the properties of the liquid lacquers relevant in terms of lacquer technology, and of the applied and dried films.

	Comparative silica 1	Silica 7	Silica 8	Reference without silica	Comparative silica 2	Silica 9	Silica 11	Reference without silica
Grindometer value [μm]	< 10	< 10	< 10	/	< 10	< 10	< 10	/
Viscosity (millibase) [mPas]								
6 rpm	409	210	220	/	5670	935	832	/
60 rpm	407	210	212	/	1260	409	407	/
Viscosity (lacquer + hardener) [mPas]								
6 rpm	120	80	80	60	446	195	175	55
60 rpm	113	82	82	61	194	146	144	64
Flow	Poor fine cracks	OK	OK	OK	Orange-peel effect	OK	OK	OK
Scratch resistance								
20° reflectometer value before scratching	81	89.5	89.1	91.3	38	85.5	85.3	91.7
Haze before scratching	101	9	12	2	423	18	19	2
40 strokes with Sikron F 500								
Residual gloss [%]	83.4	88.5	90.7	51.8	/	80.4	84.3	56.1

- The silicas 7 + 8 and 9 + 10 according to the invention can be used in high concentrations without impairing the appearance of the lacquer surface owing to their substantially lower rheological efficiency compared with comparative silica 1 and 2. In addition, the silicas according to the invention display a substantial improvement in the scratch resistance of the lacquer surface.

Example 4

- 10 Direct comparison of the silicas according to the invention with a scratch-resistant lacquer according to DE 198 11 790 A1, in which AEROSIL R 972 is used to improve the scratch resistance.

	Prior art 1)	Silicas 2) according to the invention
Millbase		
Desmophen A 2009/1		190.2
Methoxypropyl acetate: Solvesso 100 1:1		36.8
Silica		23.0
Σ		250.0
Lacquer make-up		
Desmophen A YEP4-55A, contains AEROSIL R 972	96.0	-
Millbase	-	48.9
Desmophen 2009/1	-	24.9
OL 17, 10% in MPA	-	-
Modaflow 1% in MPA	-	-
MPA : Solvesso 100 1:1	11.6	33.8
Butyl glycol acetate	10.5	10.5
Byketol OK	7.5	7.5
Byk 141	0.8	0.8
Addition of hardener		
Desmodur N 3390	23.6	23.6
Σ	150.0	150.0

Production and application of the lacquers

- 1) Comparative silica 1 is incorporated into the binder in accordance with DE 198 11 790 A1 using a jet disperser.
 - 2) The binder is mixed with the solvents. Then, for the purpose of predispersion, the silica is incorporated into this mixture with the high-speed mixer (disk Ø 45 mm) and predispersed for 5 min at 2000 rpm. The mixture is dispersed in a laboratory pearl mill for 30 min at 2500 rpm and 60% pump capacity using glass beads (Ø approx. 1 mm). The millbase is tested with a grindometer, 25 µm, according to DIN ISO 1524. It must be smaller than 10 µm.
- The conversion to lacquer of the millbases corresponding to 1) or 2) takes place in accordance with the formulation, the components being mixed at 2000 rpm with a vane agitator. The hardener is incorporated in the same way.
- After adjusting the lacquers to spray viscosity in accordance with DIN 53411, the lacquers are applied to black lacquered metal sheets, e.g. DT 36 (from Q-Panel), by spray application (coat thickness about 40-50 µm). After spraying, the metal sheets are dried for 24 h at room temperature and then for 2 h in a drying oven at 70°C.
- Scratch tests:
- The metal sheets are abraded with a CaCO₃/water slurry (100 g water + 1 g Marlon A 350, 0.25% + 5 g Millicarb CaCO₃) using an abrasion and washing resistance tester (Erichsen, brush with hog's bristles). The gloss before and 10 min after the abrading is determined with a reflectometer (20° irradiation angle).

Table 10: Summary of the properties of the liquid lacquers relevant in terms of lacquer technology, and of the applied and dried films.

	Prior art	Silica 7	Reference
Grindometer value [μm]	< 10	< 10	/
Viscosity (millbase) [mPas]			
6 rpm	58	30	30
60 rpm	48	43	40
Surface	Orange peel	OK	OK
20° reflectometer value before scratching	88.0	86.5	98.5
100 strokes with Millicarb Residual gloss [%]	88.6	96.3	59.6

5

It is shown that a substantially better improvement in the residual gloss is achieved after a scratch stressing of the lacquer surface by using the silica according to the invention than with the prior art. In addition, owing to its low rheological efficiency, the silica according to the invention does not cause an orange-peel effect.

10